Bound-Monolayer Cation Exchanger for Gas–Liquid Chromatographic Separation of cis and trans Alkenes

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The sulfobenzyl derivative of Porasil C was synthesized, converted from the H^+ to the Ag^+ form, and used for the first time as a stationary phase in gas chromatography. It showed marked selectivity for alkenes relative to alkanes. Retention times of the former were reduced by treatment of the column packing with hexamethyldisilazane and coating with ethylene glycol succinate. The resultant column packing was useful for the analytical separation of *trans*-2-hexene, *cis*-2-hexene, *trans*-2-octene, *cis*-2-octene, *trans*-5-decene, *cis*-5-decene, *trans*-3-dodecene, *cis*-3-dodecene, *trans*-7-tetradecene, *cis*-7-tetradecene, *trans*-9-octadecene, and *cis*-9-octadecene, and was stable in excess of 10 weeks at temperatures ranging from about 100–180 °C.

Silver ion-containing materials have been used to provide specific interactions with π-electron cloud systems in a variety of chromatographic approaches (*1*). Gas chromatographic applications of argentation have been limited to species of low molecular weight, because of the lack of liquid phases which provided adequate solvent power for silver compounds and which also had low volatility and high thermal stability. In gas–solid chromatography, the strong interaction of double bonds with silver ion requires elevated temperatures. For example, the elution of hexenes from columns of Chromosorb W or P impregnated with silver nitrate requires temperatures of 140–220 °C (*2*) and elution of these compounds from macroreticular ion exchange res-

Table I. Properties of Porasil and Some Surface-Bound Derivatives

Compound	% C	mequiv/gram Bound Moiety: Elemental anal.	mequiv/gram Bound Moiety: Titration	Surface area[c], m^2/g
Porasil C	...	...	0.01 (H^+)	106.0
Silica chloride[a]	...	...	0.36 (Cl^-)	...
Benzylsilica[a]	2.68	0.32	...	95.9
Sulfobenzylsilica[a]	1.58	0.19	0.16 (H^+)	111.5
Silica chloride[b]	...	...	0.41 (Cl^-)	...
Benzylsilica[b]	2.90	0.34	...	...
Sulfobenzylsilica[b]	2.13	0.25	0.25 (H^+)	...
Methylsilica	0.85	0.70	...	88.6

[a] Preparation using tribenzyltin chloride pathway. [b] Preparation using benzyl methyl ether pathway. [c] Determination by argon adsorption procedure.

ins in the Ag^+ form requires temperatures of 160–190 °C (*3*). In this work, we demonstrate the utility of a bound monolayer cation exchanger in the Ag^+ form for the separation of higher alkenes, some of which are potent insect sex attractants (pheromones) (*4*). Related stationary phase materials have been shown to be useful in liquid and thin-layer chromatography (*5*), but this is the first disclosure of their properties in gas–chromatography.

EXPERIMENTAL

Materials. Tribenzyltin chloride was prepared according to the method of Sisido (*6*) or purchased from Ventron Corporation. Methyllithium was used as a 1.65 *N* solution as supplied by Ventron Corporation. All other solvents and reagents were ACS grade or purified as described in a prior publication (*7*).

Porasil C, 80–100 mesh, Waters Associates, was Soxhlet extracted with constant boiling HCl (20.2%) until the extractant was colorless (~ 48 hr). The silica was washed until neutral on a fritted Buchner funnel, then washed several times more with acetone, followed by hexane. The air-dried silica was heated to 150 °C for 24 hr before use.

Most of the hydrocarbon solutes were purchased from Chemical Samples Company. The octenes and tetradecenes were purchased from Pfaltz and Bauer Company, and the octadecenes were synthesized in-house. Stationary phases for gas chromatography (EGS and OV-1) and hexamethyldisilazane were purchased from Applied Science Laboratories, Inc.

Syntheses. Sulfobenzyl Porasil C was synthesized using the pathway previously described (*7*). An alternate procedure was also used (*8*). It consisted of the dropwise addition of 50 mmol of methyllithium (Methyllithium must be handled cautiously. All auxiliary glassware was soaked in absolute ethanol or isopropanol before residual solid residues left by evaporation of ether could react with moisture in air.) solution to 12 mmol of tribenzyltin chloride in 200 ml of dry ethyl ether with continuous stirring. After 4 hr, the solution was cooled in an ice bath and 6 mequiv of silica chloride added. After 5 min, the bath was removed and the reaction allowed to proceed at 23 °C for 20 hr. Several times during the period, the suspension was boiled and quickly cooled to 0 °C to aid in transfer of reagent into the silica pores. The reactions were carried out in a 500-ml round-bottom flask, which was fitted with a condenser, gas inlet tube, stirrer, and dropping funnel that had been dried and flushed with dry argon before the experiment had begun. Dry argon was bled into the reaction flask throughout the procedure. The reaction mixture was acidified and the benzylsilica isolated and analyzed as described previously (*7*).

Gas Chromatography. A Varian Model 1520 gas chromatograph with hydrogen flame ionization detector was used. Columns were constructed of type 304 stainless steel tubing, 61 cm long, 1.6-mm i.d., 3.2-mm o.d. and packed for a length of 50 cm. The empty portion extended into the injection port to a point just short of the septum. Packing weights were approximately 0.5 g. Detector and injector temperatures were 267 and 244 °C, respectively. Gases were "Zero Grade" except in the cases noted where the helium carrier was of a special high purity supplied by Airco as Grade 6. It contained total impurities of 1 part per million and was particularly low in hydrogen (0.2 ppm). Carrier gas flows are reported in cm^3/min measured with a Matheson mass flowmeter, Model LF-100.

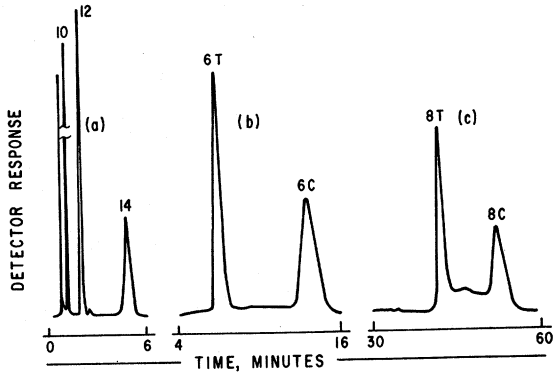

Figure 1. Chromatograms of (*a*) straight chain hydrocarbons, (*b*) *cis*- and *trans*-2-hexenes, (*c*) *cis*- and *trans*-4-octenes.

Column and conditions: silver sulfobenzyl Porasil C; column temperature, 188 °C; sample size, 1 μl of CS_2 solution containing ~10 mg/ml; helium flow rate, 20 cm^3/min; 1.2×10^{-11} A full scale (range 0.1, attenuation 4X)

Preparation of Coated GC Packings. One gram of sulfobenzyl Porasil C (0.16 mequiv/gram) was packed into 41 cm × 6.35-mm o.d., 304 stainless steel tubing, and installed in the chromatograph with the column outlet not connected to the detector. A helium flow of 30 ml/min, an injector temperature of 240 °C, and a column oven temperature of 200 °C were used, and then two 100-μl charges of hexamethyldisilazane were injected into the column in 30-min intervals. The operating conditions were then maintained for approximately 24 hr.

The silanized product was removed from the stainless steel tubing and lightly packed into a 40-cm length of 5-mm i.d. glass tubing. The following acid treatment was carried out to ensure that all the sulfobenzyl groups were in the H^+ form, since some might have been converted to the NH_4^+ form as a result of formation of NH_3 during silanization. The column packing was washed first with aliquots of 0.1 *N* HNO_3 totaling 50 ml, and then with water until the effluent was acid-free. At this point, the column was wrapped with aluminum foil to avoid reduction of Ag^+. A silver nitrate solution, 1 g $AgNO_3$ in 50 ml H_2O, was passed through the column in several aliquots totaling 50 ml. This was followed by a water wash until the effluent was free of Ag^+, as demonstrated by tests with KCl solution. A stream of dry nitrogen was passed through the column until the packing was visibly dry. Final drying, after removal from the column, was carried out in a vacuum oven at approximately 70 °C for several hours at a pressure of 150–170 mm (absolute) of dry nitrogen.

The extent of conversion to the Ag^+ form was monitored by combining the effluents from the $AgNO_3$ and subsequent water washes, adding concentrated KCl solution, filtering the AgCl on a Buchner funnel, washing the filter cake thoroughly, and titrating the free H^+ in the filtrate with 0.02 *N* NaOH.

The resulting silver sulfobenzyl Porasil C (AgSP) was coated with stationary phase using CH_2Cl_2 as the solvent.

RESULTS AND DISCUSSION

Table I indicates that similar yields of benzylsilicas were obtained regardless of which method of benzyllithium preparation was used. It has been postulated (*7*) that the lithium methylate produced by the reaction of Li with benzyl methyl ether reacts with silica chloride and is subsequently hydrolyzed, since only about 50% replacement of chloride groups is observed when Davison 62 or Syloid 72 silica chlorides are treated with benzyllithium. The extent of benzylation of macroporous silica chloride in this study has been increased to more than 80% by both pathways. Further reaction of the surface chlorides may be inhibited by steric hindrance of bound benzyl groups, although some methyl groups could also be bound in the current synthesis. To explore this further, methyllithium was reacted with silica chloride. While the error in % C determination (±0.2%) makes it impossible to say for certain that greater coverage

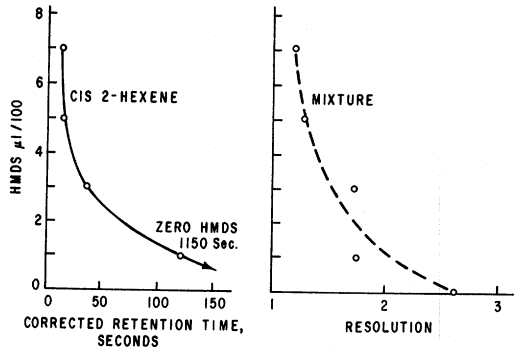

Figure 2. Effect of hexamethyldisilazane treatment on the retention time of *cis*-2-hexene and the resolution of a mixture of *cis*- and *trans*-2-hexenes on a silver sulfobenzyl Porasil C (0.16 mequiv) column with a helium carrier flow of 20 cm^3/min

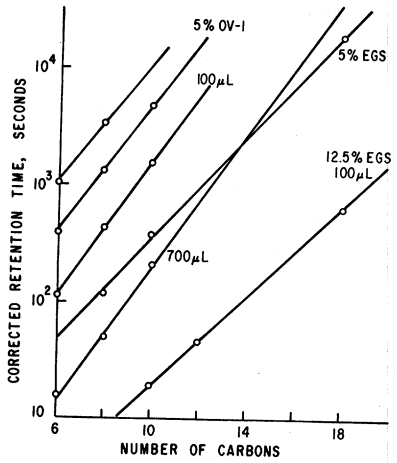

Figure 3. Variation of log corrected retention time with number of carbons in straight chain alkenes on various silver sulfobenzyl Porasil C column packings at 188 °C. Volumes indicate amount of hexamethyldisilazane used in packing preparation. Helium carrier flows, 20–30 cm^3/min

was obtained, its value and the lower surface area value [by argon adsorption determination (*9*)] indicate that fewer silanol groups remain when the methyl group is bound than when the larger benzyl group is bound. When used as packings for gas chromatography, the two types of preparations of sulfobenzyl Porasil C performed identically.

Figure 1 demonstrates that the silver form of sulfobenzyl Porasil C has a greater attraction for alkenes than alkanes, and that cis alkenes interact more strongly with the stationary phase than do their trans isomers. In contrast, hydrogen-form sulfobenzyl Porasil C does not give such selectivity or extent of retention. Retention times for homologues higher than octene on AgSP were too long to be of practical utility even though the column length was no more than 50 cm; thus a number of approaches were investigated in order to lower retention times. The abundance of surface silanol groups has been evaluated (*10*) as about 8 µmol/m^2 which is greater than the amount of sulfobenzyl groups bound to the surface in this study by a factor of 3 to 5. Only about half of the surface silanols are reactive, however (*11*). To reduce the number of free silanol groups and the extent of interaction between the stationary phase and solutes, the column was treated with hexamethyldisilazane (HMDS). Separations of cis from trans hexenes were then evaluated as depicted in Figure 2. Retention times decreased significantly as did resolution, but after 700 µl of HMDS had been added, resolution was still acceptable. (Resolution, R, was determined by the equation, $R = 2\Delta t_R/(w_a + w_b)$, where Δt_R is the difference in retention time between any two peaks a and b, and w_a and w_b are the base-line widths of the respective peaks.)

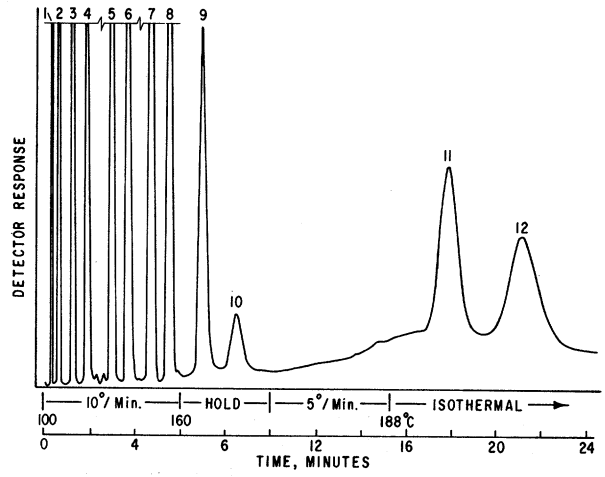

Figure 4. Chromatogram of an alkene test mixture in CS_2

Concentration, ~70 mg/ml. (1) *trans*-2-hexene, (2) *cis*-2-hexene, (3) *trans*-2-octene, (4) *cis*-2-octene, (5) *trans*-5-decene, (6) *cis*-5-decene, (7) *trans*-3-dodecene, (8) *cis*-3-dodecene, (9) *trans*-7-tetradecene, (10) *cis*-7-tetradecene, (11) *trans*-9-octadecene, and (12) *cis*-9-octadecene. Sample size, 2 µl. Column, 12.9% EGS polyester on silanized silver sulfobenzyl Porasil C. Helium (high purity) flow, 30 ml/min. 9.6 × 10^{-10} A full scale (range 1, attenuation 32×)

Table II. Analysis of a Mixture of Alkenes by GLC

	Known wt, %	Determined wt[a], %	σ
trans-2-Hexene	5.20	4.51	0.39
cis- 2-Hexene	7.64	7.35	0.23
trans-2-Octene	8.13	7.72	0.12
cis- 2-Octene	8.10	7.78	0.11
trans-5-Decene	9.37	10.77	0.14
cis- 5-Decene	9.49	9.93	0.11
trans-3-Dodecene	11.15	12.31	0.20
cis- 3-Dodecene	8.14	8.73	0.27
trans-7-Tetradecene	8.39	8.49	0.28
cis- 7-Tetradecene	2.10	1.81	0.29
trans-9-Octadecene	11.19	10.94	0.54
cis- 9-Octadecene	11.19	9.46	0.40

[a] Average of 5 determinations.

Retention times for higher alkenes were still prohibitive (Figure 3). Attempts were made to further reduce retention by coating the AgSP with typical liquid phases. A coating of 5% (w/w) OV-1 reduced retention only slightly, although a 5% (w/w) coating of EGS caused a marked reduction, presumably through the interaction of the carbonyl groups with Ag^+. Increasing the loading of EGS decreased retention with concomitant reduction of resolution similar to the trend shown in Figure 2. The best compromise was achieved with the use of a column packing which had been treated with 100 µl of HMDS and coated with 12.5% EGS. A separation based upon this column packing is depicted in Figure 4. The rather short column necessitated the use of low temperatures at the start of the elution. The climb in base line over the 160–188 °C temperature range was due to the expected bleed of EGS. The utility of the separation for analytical work may be evaluated from the accuracy and precision reported in Table II. The determined weight percent is the average of five experiments and is the area percent of the GLC peak corresponding to a particular solute. Empirical data modifiers such as response factors were not used.

Stability of the packing is adversely affected by the pres-

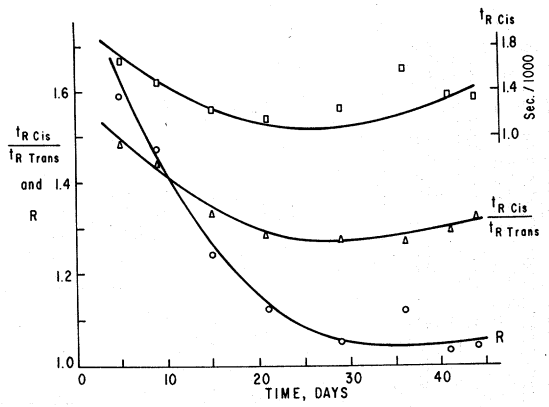

Figure 5. GC retention and resolution data for a mixture of *cis*- and *trans*-9-octadecenes on a 12.5% EGS polyester on silanized silver sulfobenzyl Porasil C column using 99.9999% helium carrier at a flow of 30 cm^3/min. Column temperature, 180 °C

ence of H_2 in the carrier gas. Zero Gas grade helium contains about 1 ppm of H_2 (*12*) which reduced the Ag^+ to Ag^0 in 10 days of operation at 180 °C under the conditions of chromatography. The packing was removed from the column, extracted with CH_2Cl_2 and Ag^0 removed with 5 *N* HNO_3. About 70% of initial capacity of the ionogenic groups remained. In order to determine the effects of H_2 in the carrier, Airco No. 6 grade helium was utilized. Each day for 44 days, over a total period of 10 weeks, two samples of a mixture of the *cis*- and *trans*-9-octadecenes were injected into the column. Figure 5 summarizes the experiment and depicts an initial decrease in retention time, relative retention, and resolution although an adequate separation was achieved throughout the course of the study. When the column was operated above 180 °C, alkene retention times decreased, but bleeding of the EGS polyester increased rapidly with temperature and loss of resolution was accelerated. When this loss of resolution becomes excessive, the column packing may be removed and regenerated as the Ag^+ form.

The extent of interaction of solutes with the surface of the supposedly inert support in GLC is often debated. On the basis of this study, there can be no doubt that the surface does interact as is evidenced by the effect of HMDS upon retention. In addition, the difference in interaction of AgSP with respect to the hydrogen-form support indicates that solutes penetrate the liquid coating and approach near to the surface. The surprising extent of coating penetration was apparent when *cis*- and *trans*-9-octadecenes were separated in 30 min at 188 °C with $R = 1.45$ on HMDS-treated AgSP at 15% loading of EGS. When a column with 20% EGS was used, a resolution of 0.57 at 180 °C was obtained. Thus, the approach described here has utility for analytical separations, provides a probe for the study of the migration of a solute through a liquid phase, and may be used to measure interactions of volatile solutes with surface-bonded groups.

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LITERATURE CITED

(1) O. K. Guha and J. Janâk, *J. Chromatogr.*, **68,** 325 (1972).
(2) J. J. Duffield and L. B. Rogers, *Anal. Chem.*, **34,** 1193 (1962).
(3) R. F. Hirsch, H. C. Stober, M. Kowblansky, F. N. Hubner, and A. W. O'Connell, *Anal. Chem.*, **45,** 2101 (1973).
(4) J. J. Vollmer and S. A. Gordon, *Chemistry*, **47,** 6 (1974).
(5) R. A. Barford, L. T. Olszewski, D. H. Saunders, P. Magidman, and H. L. Rothbart, *J. Chromatogr. Sci.*, **12,** 555 (1974).
(6) K. Sisido, Y. Takeda, and Z. Kinugawa, *J. Am. Chem. Soc.*, **83,** 538 (1961).
(7) D. H. Saunders, R. A. Barford, P. Magidman, L. T. Olszewski, and H. L. Rothbart, *Anal. Chem.*, **46,** 834 (1974).
(8) D. Seyferth, R. Suzuki, C. J. Murphy, and C. R. Sabet, *J. Organomet. Chem.*, **2,** 431 (1964).
(9) M. A. Kaiser, M. O'Brien, and R. L. Grob, *Amer. Lab.*, June–July (1975).
(10) K. Unger, *Angew. Chem., Int. Ed. Engl.*, **11,** 267 (1972).
(11) V. Y. Davydov, L. T. Zhuralev, and A. V. Kieselev, *J. Phys. Chem., USSR*, **38,** 1108 (1964).
(12) Private communication from Liquid Carbonic Corp., Dulty's Lane, Burlington, N.J. (1974).

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